

**TECHNICAL SUPPORT DOCUMENT FOR
EMISSIONS FROM PRODUCTION OF
FLUORINATED GHGS:**

**PROPOSED RULE FOR MANDATORY
REPORTING OF GREENHOUSE GASES**

Office of Air and Radiation
U.S. Environmental Protection Agency

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1. Source Description

This source category covers emissions of fluorinated greenhouse gases (fluorinated GHGs) that occur during the production of HFCs, PFCs, SF₆, NF₃, and other fluorinated GHGs such as fluorinated ethers. Specifically, it covers emissions that are never counted as “production” under the proposed requirements for suppliers of industrial greenhouse gases (discussed in Technical Support Document EPA-HQ-OAR-2008-0508-041). These emissions include fluorinated GHG products that are emitted upstream of the production measurement and fluorinated GHG byproducts that are generated and emitted either without or despite recapture or destruction. These emissions exclude generation and emissions of HFC-23 during the production of HCFC-22 (discussed in Technical Support Document EPA-HQ-OAR-2008-0508-015).

Fluorinated GHGs are man-made gases used in several sectors. They include hydrofluorocarbons (HFCs), perfluorocarbons (PFCs), sulfur hexafluoride (SF₆), nitrogen trifluoride (NF₃), and a number of fluorinated ethers, listed in Table 1. (Fluorinated greenhouse gases also include chlorofluorocarbons (CFCs) and hydrochlorofluorocarbons (HCFCs), but these ozone-depleting substances (ODSs) are currently being phased out and otherwise regulated under the Montreal Protocol and Title VI of the Clean Air Act, and EPA is not proposing requirements for them under the rule.) Hydrofluorocarbons (HFCs) are the most commonly used fluorinated GHGs, used primarily to replace ozone-depleting substances in a number of applications, including air-conditioning and refrigeration, foams, solvents, and aerosols. PFCs are used in fire fighting and to manufacture semiconductors and other electronics. Sulfur hexafluoride (SF₆) is used in a diverse array of applications, including electrical transmission and distribution equipment (as an electrical insulator and arc quencher) and in magnesium casting operations (as a cover gas to prevent oxidation of molten metal). Nitrogen trifluoride (NF₃) is used in the semiconductor industry, increasingly to reduce overall semiconductor greenhouse gas emissions through processes such as NF₃ remote cleaning and NF₃ substitution during in-situ cleaning. Fluorinated ethers (HFEs and HCFEs) are used as anesthetics (e.g., isoflurane, desflurane, and sevoflurane) and as heat transfer fluids (e.g., the H-Galdens). Fluorinated GHGs are powerful greenhouse gases whose ability to trap heat in the atmosphere is often thousands to tens of thousands as great as that of CO₂, on a pound-for-pound basis. Some fluorinated GHGs are also very long lived; SF₆ and the PFCs have lifetimes ranging from 3,200 to 50,000 years (IPCC, 2006).

Fluorinated GHGs can escape during the production process. Emissions can occur from leaks at flanges and connections in the production line, during separation of byproducts and products, during occasional service work on the production equipment, and during the filling of tanks or other containers that are distributed by the producer (e.g., on trucks and railcars). As discussed further below, the quantities emitted quantities are estimated on a regular basis (e.g., daily, weekly, monthly) through mass balance calculations and physical process measurements taken (e.g. weight, flow rates). These emission data then become part of the basis for plant and plant site Title V emission permit applications. Fluorinated GHG emissions from U.S. facilities producing fluorinated GHGs are estimated to range from 0.8 percent to 2 percent of the amount produced, depending on the facility.

a. Total U.S. Production and Associated Emissions

In 2006, 12 U.S. facilities collectively produced over 350 million metric tons of carbon-dioxide equivalent (mtCO₂e) of HFCs, PFCs, SF₆, and NF₃. At an emission rate of 1.5%, these facilities together would have emitted approximately 5.4 million mtCO₂e of HFCs, PFCs, SF₆, and NF₃. This total breaks down into estimated emissions of almost 4 million mtCO₂e of HFCs, about 210,000 mtCO₂e of PFCs, approximately 700,000 mtCO₂e of SF₆, and just over 500,000 mtCO₂e of NF₃. EPA estimates that an additional six facilities collectively produced almost 1 million mtCO₂e of fluorinated anesthetics. At an emission rate of 1.5%, these facilities together would have emitted approximately 15,000 mtCO₂e of fluorinated anesthetics.

2. Options for Reporting Threshold

EPA evaluated a range of threshold options for fluorinated GHG production facilities. These included emissions thresholds of 1,000 mtCO₂e, 10,000 mtCO₂e, 25,000 mtCO₂e and 100,000 mtCO₂e and their capacity equivalents. Facility-specific emissions were estimated by multiplying an emission factor of 1.5 percent by the estimated production at each facility. The capacity thresholds were developed based on emissions of fluorinated GHGs, assuming full capacity utilization and an emission rate of 2 percent of production. Because EPA had little information on combustion-related emissions at fluorinated GHG production facilities, these emissions were not incorporated into the capacity thresholds or the threshold analysis.

Table 1 illustrates the HFC, PFC, SF₆, and NF₃ emissions and facilities that would be covered under these various thresholds.

Table 1. Threshold Analysis for Emissions from Production of HFCs, PFCs, SF₆, and NF₃

Emission Threshold Level	Total National Emissions (mtCO ₂ e)	Number of Facilities	Emissions Covered		Facilities Covered	
			mtCO ₂ e	Percent	Number	Percent
1,000	5,300,000	12	5,300,000	100%	12	100%
10,000	5,300,000	12	5,300,000	100%	12	100%
25,000	5,300,000	12	5,300,000	100%	12	100%
100,000	5,300,000	12	5,100,000	97%	9	75%

Capacity Threshold Level	Total National Emissions (mtCO ₂ e)	Number of Facilities	Emissions Covered		Facilities Covered	
			mtCO ₂ e	Percent	Number	Percent
50,000	5,300,000	12	5,300,000	100%	12	100%
500,000	5,300,000	12	5,300,000	100%	12	100%
1,250,000	5,300,000	12	5,300,000	100%	12	100%
5,000,000	5,300,000	12	5,200,000	98%	10	83%

As can be seen from the tables, most HFC, PFC, SF₆, and NF₃ production facilities would be covered by all emission- and capacity-based thresholds. All facilities producing HFCs, PFCs, SF₆, and NF₃ have capacities above 1,250,000 mtCO₂e, the capacity equivalent to an annual emissions rate of 25,000 mtCO₂e, assuming full capacity utilization and a 2% emission rate. Although EPA does not have facility-specific production capacity information for producers of fluorinated anesthetics, EPA believes that few or none of these facilities are likely have capacities above that threshold.

Where EPA has reasonably good information on the relationship between production capacity and emissions, and where this relationship does not vary excessively from facility to facility, EPA is generally proposing capacity-based thresholds to make it easy for facilities to determine whether or not they must report. In this case, however, EPA has little data on combustion emissions and their likely magnitude compared to fluorinated GHG emissions from this source.

As noted above, the capacity thresholds in Table 1 were developed based on a fluorinated GHG emission rate of 2 percent of production. While EPA believes that this emission rate is an upper-bound for fluorinated GHGs, neither the rate nor the thresholds account for combustion-related emissions. Thus, it is possible that the production capacities listed in Table 1 are inappropriately high.

In the event that a capacity-based threshold were adopted, facilities could be required to multiply the production capacity of each production line by the GWP of the fluorinated GHG produced on that line. Facilities could then be required to sum the resulting CO₂e capacities across all lines. Where more than one fluorinated greenhouse gas could be produced by a production line, yielding more than one possible production capacity for that line in CO₂e terms, facilities could be required to use the highest possible production capacity (in CO₂e terms) in their threshold calculations. This would ensure that facilities that had the potential to emit more than the threshold quantity would be required to report.

3. Monitoring Methods and Current Plant Practices

In developing the proposed rule, EPA reviewed a number of protocols for estimating fluorinated GHG emissions from fluorocarbon production, such as the 2006 IPCC Guidelines. In general, these protocols present three methods. In the first method, a default emission factor is applied to the total production of the plant. In the second method, emissions are equated to the difference between the mass of reactants fed into the process and the sum of the masses of the main product and those of any byproducts and/or wastes. In the third method, the composition and mass flow rate of the gas streams actually vented to the atmosphere are monitored either continuously or during a period long enough to establish an emission factor.

a. First Method: Default Emission Factor

Although the first approach is simple, it is also highly imprecise; emissions of fluorinated GHG products in U.S. plants are estimated to vary from 0.8 percent to 2 percent of production, more than a factor of two (RTI, 2008).¹ Thus, applying a default factor (1.5 percent, for example) is likely to significantly overestimate emissions at some plants while significantly underestimating them at others.

b. Second Method: Mass-balance

In the mass-balance approach, also known as the yield approach, facilities weigh or meter the reactants fed into the process, the product resulting from the process, and any byproducts and wastes that are removed from the process (i.e., sent to the thermal oxidizer or other equipment, not immediately recycled back into the process). Facilities then calculate the difference between the mass of reactants fed into the process and the sum of the masses of the main product and those of any byproducts and/or wastes. This difference is then assigned to loss of reactants, loss of product, and/or conversion to byproducts.

Because the mass-balance approach relies on the calculation of relatively small differences between relatively large numbers, measurements must have good precision to avoid large uncertainties in the emissions estimates. For example, if the masses of reactants, products, and wastes are measured with a precision of ± 1 percent, and the emissions rate is equivalent to 1.5 percent of production, the error in the emissions estimate will be ± 93 percent in relative terms. For an average-size facility, this equates to an absolute uncertainty of over $\pm 400,000$ mtCO₂e. With an accuracy and precision² of ± 0.2 percent in the mass measurements, the error in the emissions estimate for a 1.5 percent emission rate will be 20 percent, which equates to an absolute uncertainty of about 90,000 mtCO₂e for an average-size facility.

As discussed further below, it is EPA's understanding that plants already perform these measurements and calculations to monitor their processes and yields, and EPA therefore believes that the mass-balance method would not impose an undue burden.

¹ The emission rates cited were estimated for HCFC-22, which is an ozone-depleting substance and therefore excluded from the proposed rule. However, the production processes for many fluorinated GHGs are similar to those for HCFC-22 (2006 IPCC Guidelines, Volume 3, section 3.10.2.1), and therefore their emission rates are likely to be similar as well.

² Multiple—e.g., daily—measurements can increase the precision of monthly and annual totals, but they will not increase their accuracy. Thus, the precision requirements for a daily measurement can be relaxed below the requirements for the annual total. However, the accuracy requirements for a daily measurement cannot be relaxed below the requirements for the annual total.

There are two variants of the mass-balance method. In the first variant, only some of the reactants and products, including the fluorinated GHG product, are considered. In the second variant, all of the reactants, products, and byproducts are considered.

1. Mass-balance: Variant 1

The first variant of the mass-balance method is implemented by calculating the difference between the expected production of each fluorinated GHG based on the consumption of reactants and the measured production of that fluorinated GHG, accounting for yield losses related to byproducts and wastes. Yield losses that cannot be accounted for are attributed to emissions of the fluorinated GHG product. This calculation is performed for each reactant, and estimated emissions of the fluorinated GHG product are equated to the average of the results obtained for each reactant. If fluorinated GHG byproducts are produced and are not completely recaptured or completely destroyed, emissions of each fluorinated GHG byproduct are also estimated. (By-products may include end-products of the reaction [other than the main product] and intermediates that are permanently removed from the process.)

The advantage of this approach is that it ignores losses that cannot be losses of the fluorinated GHG product. For example, some fluorocarbons are produced by reacting an organic (carbon-containing) compound with HF, ultimately producing the fluorinated GHG and HCl. By paying attention only to the carbon- or fluorine-containing compounds, one can disregard possible losses of HCl as a source of the calculated process losses.

This approach is similar to the mass-balance approach described in the 2006 IPCC Guidelines for fluorochemical production. (The approach is mentioned in section 3.10.2, which describes general methods for estimating emissions from fluorinated GHG production, but it is discussed in more detail in section 3.10.1, which describes methods for estimating HFC-23 emissions from HCFC-22 production.) In that approach, fluorine and carbon “balance efficiencies” are used to estimate emissions of fluorinated GHG products and byproducts. The balance efficiency is the fraction of the mass of an element that was contained in the reactants for a process that is contained in the products of that process. The balance efficiency can be calculated from the masses, molecular weights, and stoichiometric coefficients of the reactants and products that contain the balanced element as follows:

$$BE = \frac{P * MW_R * SC_R}{R * MW_P * SC_P}$$

where:

BE	=	the balance efficiency of the process for the balanced element (fraction)
P	=	the total mass of the fluorinated GHG produced over the period p (metric tons)
R	=	the total mass of the reactant that contains the balanced element and that is consumed in the process over the period p (metric tons)
MW _R	=	the molecular weight of the reactant containing the balanced element
MW _P	=	the molecular weight of the fluorinated GHG produced
SC _R	=	the stoichiometric coefficient of the reactant containing the balanced element
SC _P	=	the stoichiometric coefficient of the fluorinated GHG produced

Although the mass-balance approach outlined in the equations below does not use the quantity “balance efficiency” as presented here, it uses the logic behind it. That is, it compares the quantity of the product that is actually measured to the quantity of the product that should theoretically have been created by the quantity of reactants consumed.

To estimate emissions, the Guidelines recommend using the average of both the carbon and fluorine calculations unless the uncertainty of one is significantly lower than that of the other; in this case, the Guidelines recommend that the calculation with the lower uncertainty be used.

The following set of equations summarizes the element-balancing method for estimating fluorinated GHG emissions.

Equation 1a estimates the total mass of fluorinated GHGs emitted annually from the production process, based on production over multiple days or shorter periods. (This equation is also used in the second approach.)

$$E_p = \sum_{p=1}^n \sum_i E_{pip} \quad (\text{Eq.1a})$$

Where:

- E_p = The total mass of each fluorinated GHG product emitted annually from all production processes (metric tons)
- E_{pip} = The total mass of the fluorinated GHG product emitted from production process i over the period p (metric tons, defined in Equation L-3)
- p = period over which mass flows and concentrations are measured
- n = Number of concentration and flow measurement periods for the year

Equation 2a estimates the total mass of fluorinated GHG byproduct k emitted annually from all fluorinated GHG production processes:

$$E_{Bk} = \sum_{p=1}^n \sum_i E_{Bkip} \quad (\text{Eq.2a})$$

where:

- E_{Bk} = the total mass of fluorinated GHG byproduct k emitted annually from all production processes (metric tons)
- E_{Bkip} = the total mass of fluorinated GHG byproduct k emitted from production process i over the period p (metric tons, defined in Equation L-8)
- p = period over which mass flows and concentrations are measured
- n = Number of concentration and flow measurement periods for the year

Equation 3a calculates the total mass of each fluorinated GHG product emitted from production process i over the period p. This calculation is performed for each reactant, and estimated emissions are equated to the average of the results obtained for each reactant.

$$E_{Pip} = \frac{R * MW_P * SC_P}{MW_R * SC_R} - P - \sum_j (c_P * W_{Dj}) - \sum_k L_{Bkip} \quad (\text{Eq.3a})$$

where:

- E_{Pip} = the total mass of each fluorinated GHG product emitted from production process i over the period p (metric tons)
- P = the total mass of the fluorinated GHG produced by production process i over the period p (metric tons)
- R = the total mass of the reactant that is consumed by production process i over the period p (metric tons, defined in Equation 4a)
- MW_R = the molecular weight of the reactant
- MW_P = the molecular weight of the fluorinated GHG produced
- SC_R = the stoichiometric coefficient of the reactant
- SC_P = the stoichiometric coefficient of the fluorinated GHG produced
- c_P = the concentration (mass fraction) of the fluorinated GHG product in stream j of destroyed wastes. If this concentration is only a trace concentration (less than 0.1 percent by weight of the process stream), c_P is equal to zero.
- W_{Dj} = the mass of wastes removed from production process i in stream j and destroyed over the period p (metric tons, defined in Equation 5a)
- L_{Bkip} = yield loss related to byproduct k for production process i over the period p (metric tons, defined in Equation 6a)

For reference purposes, Equation 3a can be rewritten in terms of the Balance Efficiency as follows:

$$E_{Pip} = (1 - BE) * \frac{R * MW_P * SC_P}{MW_R * SC_R} - P - \sum_j (c_P * W_{Dj}) - \sum_k L_{Bkip}$$

To ensure consistency between the fluorinated GHG emissions category and the industrial gas supply source category (i.e., avoid double-counting or overlooking emissions), the total mass of fluorinated GHGs produced in Equation 3a should be estimated using the same methods and measurements used to measure production for the industrial gas supply source category.

Equation 4a estimates the total mass of the reactant that contains the balanced element and that is consumed over the period p. It accounts for the fact that some fraction of the tracked reactant may remain unreacted.

$$R = R_F - R_R \quad (\text{Eq.4a})$$

Where:

- R = total mass of the reactant that is consumed by production process i over the period p (metric tons)
- R_F = total mass of the reactant that is fed into production process i over the period p (metric tons)
- R_R = total mass of the reactant that is permanently removed from production process i over the period p (metric tons)

Equation 5a estimates the total mass of the wastes removed from the process and destroyed over the period p:

$$W_{Dj} = W_{Fj} * DE \quad (\text{Eq. 5a})$$

Where:

- W_{Dj} = the mass of wastes removed from production process i in stream j and destroyed over the period p (metric tons)
- W_{Fj} = the total mass of wastes removed from production process i in stream j and fed into the destruction device over the period p (metric tons)
- DE = Destruction Efficiency of the destruction device (fraction)

Equation 6a estimates the yield loss related to byproduct k for production process i over period p. The term is derived by considering how much product is prevented from forming by the formation of the byproduct, which competes for one of the elements in the reactant. (If a byproduct does not compete for one of the elements in the reactant, then it need not be considered in this variant of the mass-balance approach.)

$$L_{Bkip} = \frac{(B_{kip} * MW_P * ME_{Bk})}{(MW_{Bk} * ME_P)} \quad (\text{Eq. 6a})$$

Where:

- L_{Bkip} = Yield loss related to byproduct k for production process i over the period p (metric tons)
- B_{kip} = the mass of byproduct k generated by production process i over the period p (metric tons, defined in equation L-7)
- MW_P = the molecular weight of the fluorinated GHG produced
- MW_{Bk} = the molecular weight of byproduct k

- ME_{Bk} = the moles of the element shared by the reactant, product, and byproduct k per mole of byproduct k
- ME_P = the moles of the element shared by the reactant, product, and byproduct k per mole of the product

If byproduct k is responsible for yield loss in production process i and occurs in any process stream in more than trace concentrations, the mass of byproduct k generated by production process i over the period p is estimated using equation 7a below:

$$B_{kip} = \sum_j c_{Bkj} * S_j \quad (\text{Eq. 7a})$$

Where:

- B_{kip} = the mass of byproduct k generated by production process i over the period p (metric tons)
- c_{Bkj} = the concentration (mass fraction) of the byproduct k in stream j of production process i over the period p. If this concentration is only a trace concentration, c_{Bkj} is equal to zero.
- S_j = the mass flow of process stream j of production process i over the period p

If byproduct k is responsible for yield loss, is a fluorinated GHG, occurs in any process stream in more than trace concentrations, and is not completely recaptured or completely destroyed, the total mass of byproduct k emitted from production process i over the period p is estimated using equation 8a below:

$$E_{Bkip} = B_{kip} - \sum_j c_{Bkj} * W_{Dj} - \sum_l c_{Bkl} * S_{Rl} \quad (\text{Eq. 8a})$$

Where:

- E_{Bkip} = the mass of byproduct k emitted from production process i over the period p (metric tons)
- B_{kip} = the mass of byproduct k generated by production process i over the period p (metric tons)
- c_{Bkj} = the concentration (mass fraction) of the byproduct k in stream j of destroyed wastes over the period p. If this concentration is only a trace concentration, c_{Bkj} is equal to zero.
- W_{Dj} = the mass of wastes that are removed from production process i in stream j and that are destroyed over the period p (metric tons, defined in Equation L-5)
- c_{Bkl} = the concentration (mass fraction) of the byproduct k in stream l of recaptured material over the period p. If this concentration is only a trace concentration, c_{Bkl} is equal to zero.

S_{RI} = the mass of materials that are removed from production process i in stream l and that are recaptured over the period p

The last two equations require quantification of byproduct generation and emissions if a byproduct occurs in more than trace concentrations in any stream. Another approach would be to require quantification of byproduct generation and emissions only if the byproduct accounted for yield losses of more than a certain amount, e.g., 0.2 percent. Under Variant 1 of the mass-balance method, ignoring yield losses would increase the estimate of the fluorinated GHG product emitted from the process. This would lead to an overestimate of fluorinated GHG emissions if the byproduct (or product) in the ignored process stream were ultimately destroyed or recaptured. If a byproduct in an ignored process stream were ultimately emitted, then emissions of that byproduct would be attributed to the product instead. This could lead either to an overestimate or to an underestimate of CO₂-equivalent emissions, depending on the tons of product lost per ton of byproduct generated and the relative GWPs of the byproduct and product.

Variant 1 as a whole assumes that all yield losses that are not accounted for are attributable to emissions of the fluorinated GHG product. In some cases, the losses may be untracked emissions or other losses of reactants or fluorinated by-products. In general, EPA understands that reactant flows are measured at the inlet to the reactor; thus, any losses of reactant that occur between the point of measurement and the reactor are likely to be small. However, reactants that are recovered from the process, whether they are recycled back into it or removed permanently, may experience some losses that Variant 1 does not account for.

Fluorocarbon by-products, according to the IPCC Guidelines, generally have “radiative forcing properties similar to those of the desired fluorochemical.” If this is generally the case, then assuming by-product emissions are product emissions will not lead to large errors in estimating overall fluorinated GHG emissions.³ If the GWPs of emitted fluorinated by-products are sometimes significantly different from those of the fluorinated GHG product, and if the quantity of by-product emitted can be estimated (e.g., based on periodic or past sampling of process streams), then the quantity of emitted products and byproducts could be adjusted to reflect this.

2. Mass-balance: Variant 2

The following set of equations summarizes the second variant of the mass-balance method for estimating fluorinated GHG emissions, based on the total mass lost during the reaction. In this variant, as in the first, losses of reactants and byproducts that contain the element balanced in Variant 1 may be counted as losses of the fluorinated GHG product. However, in addition, losses of reactants and products that do not contain the balanced element may be counted as losses of the fluorinated GHG product. Thus, this variant is less precise than the first and has more potential to overestimate emissions.

³ Conversations with producers of fluorinated GHGs indicate that the GWPs of the product and various byproducts can be significantly different, in one case differing by more than a factor of 10. This case is in addition to the case of HFC-23 generated from HCFC-22 production, which is discussed in Technical Support Document EPA-HQ-OAR-2008-0508-015.

Equation 1b is the same as Equation 1a above.

Equation 2b estimates the total mass of fluorinated GHGs emitted from the production process over the period p.

$$E_p = R_p - (P_p + B_{NON-GHG}) \quad (\text{Equation 2b})$$

Where:

E_p = the total mass of fluorinated GHG emitted

R_p = the total mass of the reactants fed into the process over the period p (metric tons)

P_p = the total mass of the fluorinated GHG produced over the period p (metric tons)

$B_{NON-GHG}$ = the total mass of the non-GHG reactants or byproducts permanently removed from the process over the period p (metric tons)

Equation 3b estimates the total mass of non-GHG reactants or byproducts removed from the process over the period p.

$$B_{NON-GHG} = M - B_{GHG} - P_{GHG} \quad (\text{Equation 3b})$$

Where:

$B_{NON-GHG}$ = total mass of non-GHG reactants or byproducts removed from the process over the period p

M = total mass of materials permanently removed from the production process (other than the main product stream)

B_{GHG} = mass of GHG reactants or byproduct(s) permanently removed and released

P_{GHG} = mass of GHG products(s) permanently removed along with non-GHG reactants or byproducts and released

Equation 4b estimates the total mass of GHG product permanently removed and released.

$$P_{GHG} = c_{PGHG} * F_M \quad (\text{Equation 4b})$$

Where:

P_{GHG} = total mass of the GHG product removed and released

c_{PGHG} = concentration (mass fraction) of GHG product in the process stream of materials permanently removed from the production process and partly or completely released

F_M = mass flow of process stream containing materials permanently removed from the production process and partly or completely released

Equation 5b estimates the total mass of GHG byproducts permanently removed and released.

$$B_{GHG} = c_{BGHG} * F_M \quad \text{(Equation 5b)}$$

Where:

B_{GHG} = total mass of the GHG product removed and released

C_{BGHG} = concentration (mass fraction) of GHG byproduct in the process stream of materials permanently removed from the production process and partly or completely released

F_M = mass flow of process stream containing materials permanently removed from the production process and partly or completely released

c. *Third Method: Monitoring of Process Vents*

In the third method for estimating fluorinated GHG emissions, the composition and mass flow rate of the gas streams actually vented to the atmosphere are monitored either continuously or during a period long enough to establish an emission factor. (This emission factor would relate emissions to production or to consumption of reactants.) The 2006 IPCC Guidelines state that such monitoring yields more precise results than the mass-balance approach, but the Guidelines do not provide a quantitative estimate of the improvement in precision.

Based on discussions with industry manufacturers (explained further below), plants do not routinely monitor their process vents, and therefore such monitoring is likely to be more expensive than the mass-balance approach. However, the cost of monitoring may not be prohibitive, particularly if it is performed for a relatively short period of time for the purpose of developing an emission factor. Moreover, if the vent monitoring approach reduces the uncertainty of the emissions measurement by even 10% relative to the mass-balance approach, this would reduce the absolute uncertainty at the typical production facility by 40,000 metric tons CO₂e. (The extent to which uncertainty would be reduced would depend in part on the sensitivity and precision of the vent concentration measurements.)

For completeness, monitoring of process vents would need to be supplemented by monitoring of equipment leaks, whose emissions would not occur through process vents. To capture emissions from equipment leaks, EPA Method 21 and the *Protocol for Equipment Leak Estimates* (EPA-453/R-95-017) could be used. The *Protocol* includes four methods for estimating equipment leaks. These are, from least to most accurate, the Average Emission Factor Approach, the Screening Ranges Approach, the EPA Correlation Approach, and the Unit-Specific Correlation Approach. Most recent EPA leak detection and repair regulations require use of one of the Correlation Approaches in the *Protocol*. To use any approach other than the Average Emission Factor Approach, facilities would need to have (or develop) Response Factors relating concentrations of the target fluorinated GHG to concentrations of the gas with which the leak detector was calibrated. At least two fluorocarbon producers currently use methods in the *Protocol* to quantify their emissions of fluorinated GHGs with different levels of accuracy.⁴

⁴ One producer estimates HFC and other fluorocarbon emissions by using the Average Emission Factor Approach. This approach simply assigns an average emission factor to each component without any evaluation of whether or how much that component is actually leaking. The second producer estimates emissions using the Screening Ranges Approach, which assigns different emission factors to components based on whether the concentrations of the target chemical are above or below 10,000 ppmv. This producer has developed a Response Factor for HCFC-22, which is

d. Current Plant Practices

Industry representatives from leading manufacturers were contacted on several occasions, throughout the scope of this assessment project, to ascertain current plant practices as they related to:

- general process flow streams; and
- quantitative techniques for measuring production of finished product produced, various by-product streams, waste streams, common practices, and the ability to measure process emissions.

The current best practices of the fluorinated gas industry include accurate monitoring techniques, reducing the burden of a rule. While production itself is to be reported and is discussed in a separate technical support document (EPA-HQ-OAR-2008-0508-041), product weight is one element of the emissions calculations; thus, the measurement of product weight is discussed below.

Production yield is measured by reconciling the following streams in the process:

- measure of reactants into the reactor
- measure of waste or by-product
- measure of “finished product” collected
- amount of process losses, including emissions lost during manufacturing and during loading and transfer of finished product to customer storage tanks.

Mass and mass flow monitoring

During product manufacturing, plants may use either weigh scales/load cells (a load cell is the actual “weight sensor” mechanism within a weigh scale) or flowmeters to measure the quantities of materials passing through various points in the production line. Production facilities may use either technique as their primary means of quantification (weight or flow rates). Typically if facilities use weigh scales as their primary measure of production, they will use flowmeters as a secondary measure and vice-versa.

Weigh scales provide a reliable, repeatable, and accurate weight of fluorinated GHGs. Typical “weigh scale accuracy” published by leading manufacturers, and acknowledged by users, is +/- 0.02-0.05%. Many specifications for bulk industrial weighing, tank/vessel weighing, and truck loading are accurate to published +/- 0.03-0.04% figures and verified by manufacturers. It is good practice to calibrate weigh scales every 6 months or sooner if general maintenance is scheduled or if there is a reason to expect error from the monthly reconciliation reports filed to the business.

Flowmeters are commonly used by some manufacturers for process control as reactants enter the reactor, and as product enters each tank. Exact flowmeter locations can be:

- in lines measuring reactants loading the reactor
- in the lines of waste / by-products

present in the same streams as the HFC-23 whose leaks are being estimated. (HFC-23 emissions are discussed in a separate Technical Support Document.)

- in the line leading to the “day tank,” measuring daily finished product manufactured

Even when these flow meters are not primarily used to estimate production, they can be used for secondary production checks. Flow of pure HFC into the day tank can be collected on a daily basis. Flow meters are not placed as product is released from the reactor, as it has yet to go through the purification / distillation process. As such, the first true point in the process where measurements of a purified product without impurities can be taken is just prior to entering the “day tank”.

The most accurate type of flowmeter is the Coriolis flowmeter. An advantage of Coriolis flowmeters is that it measures the mass flow rate directly, which eliminates the need to compensate for changing temperature, viscosity, and pressure conditions. Coriolis flowmeters can be purchased with accuracies quoted through specifications at $\pm 0.15\%$, however, the more common flowmeter accuracy for industry-wide use approaches $\pm 0.5\%$. Flow meters are calibrated every 6-12 months unless there is a reason to suspect error coming from a mass balance and yield check that is done daily and reconciled monthly per product.

Pro and cons to Coriolis flowmeters are as follows:

Pros:

- Higher accuracy than most flowmeters;
- Can be used in a wide range of liquid flow conditions;
- Capable of measuring hot and cold fluid flow;
- Low pressure drop; and
- Suitable for bi-directional flow

Cons:

- High initial set up cost;
- Clogging may occur and difficult to clean;
- Larger in over-all size compared to other flowmeters; and
- Limited line size availability.

Whatever type of measurement device they use, fluorinated GHG producers track production at each stage of the production process. Daily and monthly mass balance is usually completed for each product produced. Percent yield is a very important for the fluorinated GHG producers; it represents the amount of starting materials used, minus byproducts and other impurities (e.g., unreacted reactants) removed from the process, minus losses which are unaccounted for, yielding an amount of prime final product which is available for sale. This calculation is commonly done on a daily basis and then reconciled monthly with product sales. In order to estimate the total amount of pure HFC produced, this calculation must be performed using the weights of the starting materials used, minus the weight of byproducts and other impurities removed from the process; the remainder of the total mass should be assumed to have been produced, and will equal the final product available for sale plus any unaccounted for losses. Mass balance calculations will be specific to each HFC finished product and manufacturing process. (The mass

balance equation used for calculations is the same; however, product molecular weight differences necessitate specific calculations.)

Fluorinated GHG emissions can be calculated from the mass balance and percent yield figures. In general, losses are a function of the number of flanges, hoses, and connections present in the production line and needed to fill trucks and railcars, as well as the number of vessels filled on a monthly basis. Flanges are typically checked for leaks on a quarterly basis. As noted above, typical losses are estimated to range from 1-2% through manufacturing, delivery and unloading to customer storage tanks at end-user facilities. In general, it is good practice to minimize flanges and connections, since each one becomes a potential source of emissions.

Monitoring of Waste Streams and Process Vent Emissions

When a new process is installed or a plant is built, manufacturers will typically conduct analyses of all product streams and process vent emissions. This is done to ensure the process can be run at steady-state, achieve acceptable yields and overall perform to scale-up expectations. The same holds true for process vents and emissions. Manufacturers need to know emissions in order to accurately apply for Title V emission permits for each plant and site. (As noted above, some manufacturers also estimate emissions from process equipment using methods from EPA's *Protocol for Equipment Leak Estimates*).

Industry representatives were consulted for common practices employed today, during routine manufacturing, for measuring and monitoring process waste streams and emissions.

Analytical technology exists, through the use of gas chromatography, to determine the concentration of fluorinated greenhouse gases in process streams. When the technique is employed, gas chromatographs are generally calibrated using certified standards with known concentrations of the same chemical(s) in the same range(s) (fractions by mass) as the process samples. Calibration gases are prepared from a high-concentration certified standard using a gas dilution system that meets the requirements specified in Test Method 205, 40 CFR Part 51.

This monitoring of product streams and emissions is not generally done on a regular manufacturing basis. It would add extra cost and have little benefit on a normal production basis. The one exception is on the manufacture of very expensive materials, where it is economically justified to account for every pound produced. Manufacturers can and will monitor in order to conduct process trouble-shooting when and if needed. Industry representatives once again reaffirmed, that there is no hard and fast rule on frequency or when to employ the gas chromatography analytical monitoring described above.

HFC manufacturers discussed typically having between 1 and 5 point source emission vents per full-scale process. Acid scrubbers are typically utilized at appropriate process points before venting. Product emissions from distillation column vents can be measured, while trace quantities coming from incomplete thermal oxidation are more challenging analytically.

4. Procedures for Estimating Missing Data

In the event that a scale or flowmeter normally used to measure reactants, products, byproducts, or wastes fails to meet an accuracy test, malfunctions, or is rendered inoperable, facilities could be required to estimate these quantities using other measurements where those are available. For example, facilities that ordinarily measure production by metering the flow into the day tank could use the weight of product charged into shipping containers for sale and distribution. EPA's

understanding is that the types of flowmeters and scales used to measure fluorocarbon production (e.g., Coriolis meters) are generally quite reliable, and therefore that it should rarely be necessary to rely solely on secondary production measurements. In general, production facilities rely on accurate monitoring and reporting of the inputs and outputs of the production process.

If concentration measurements are unavailable for some period, facilities could use the average of the concentration measurements from just before and just after the period of missing data.

If either method would result in a significant under- or overestimate of the missing parameter, the facility could be required to develop an alternative estimate of the parameter and explain why and how it developed that estimate. The advantages of such a provision are that it would add flexibility to the rule and could improve emission estimates in the event of missing data. The disadvantages are that it would add complexity to the rule, and EPA may find it difficult to confirm the soundness and accuracy of alternative methods and estimates.

5. QA/QC Requirements

Typical QA/QC requirements for measuring devices include initial and periodic verification and calibration. (For example, see the requirements of EPA's Acid Rain regulations at 40 CFR Part 75.) In this case, it may be appropriate to require an initial verification of flowmeters and weigh scales and periodic calibration in accordance with the applicable industry standards. Calibration of flowmeters and scales could be performed prior to the reporting year; after the initial calibration, recalibration could be performed at least annually or more frequent if specified by the manufacturer. Under this approach, producers could perform the verification and calibration of their weigh scales during routine product line maintenance.

For the gas chromatography analytical method described under the monitoring section of this document, monthly calibration, using known certified standards should be used. The calibration involves validating accurate measurement of these fluorocarbon standards across a range of possible concentrations, depending on which process streams are being measured.

6. Reporting and Recordkeeping Procedures

Reporting of the following data (by chemical and process, in metric tons) would be useful for confirming emissions calculations and/or calculating emission rates that could be compared across facilities and over time for data quality control purposes:

- total mass of each fluorinated GHG emitted from the fluorinated GHG production process.
- total mass of the fluorinated GHG produced
- total mass of each reactant fed into the production process
- total mass of each reactant permanently removed from the production process
- total mass of the fluorinated GHG product removed from the production process and destroyed,
- total mass of each byproduct generated,
- total mass of each byproduct destroyed at the facility,

- total mass of each byproduct recaptured and sent off-site for destruction, and
- total mass of each byproduct recaptured for other purposes.

Owners and operators of facilities producing fluorinated GHGs could be required to retain records documenting the data reported, including records of daily and monthly mass-balance calculations and calibration records for flowmeters, scales, and gas chromatographs. These records would be useful for verifying that the GHG emissions monitoring and calculations were performed correctly.

7. References

IPCC (2006) 2006 IPCC Guidelines for National Greenhouse Gas Inventories. The National Greenhouse Gas Inventories Programme, The Intergovernmental Panel on Climate Change, H.S. Eggleston, L. Buendia, K. Miwa, T. Ngara, and K. Tanabe (eds.). Hayama, Kanagawa, Japan.

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RTI International. "Verification of Emission Estimates of HFC-23 from the Production of HCFC-22: Emissions from 1990 through 2006." March 2008.

Product Websites:

Coriolis flow meters:

Micro Motion: www.emersonprocess.com/MicroMotion/

Siemens: <https://pia.khe.siemens.com/index7625.htm>

Weigh Scales / Weigh Cells

Mettler Toledo: www.mt.com or

http://us.mt.com/mt/filters/products-applications_industrial-weighing/

American Weigh Scales: www.americanweigh.com